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This brief Note dwells on the possibility of using experimental data to separate the effects of molecular reorientation on Raman bandshapes from other line-broadening contributions.

Keywords: Spectroscopy, Raman spectroscopy, IR spectroscopy, Linewidth, Lineshape, Molecular reorientation

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Raman Band Shapes and Molecular Reorientation

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Although it has been known for some time¹⁻³ that vibrational Raman bands are sensitive to the molecular reorientation in liquids, dense gases, and certain types of solids, it has not been quite clear whether and to which extent would other broadening mechanisms interfere with the determination of the tensor reorientation correlation function $\chi_2(\tau)$ from Raman data.

About a year ago I developed⁴ an evaluation method which leads to a reliable determination of $\chi_2(\tau)$ under very general circumstances. A practically identical method has been presented independently by Bartoli and Litovitz⁵ and used in their recent study of a number of liquids. Because of this important experimental confirmation of the validity of the method, I would like to make a short remark on those of my results which either have still not been published or which, in my opinion, have not been stressed enough by other authors.

The method can be described as follows. Consider a Raman band connected with the vibrational transition $r \rightarrow s$ and denote as $I_{rs}^{\parallel}(\omega)$ and $I_{rs}^{\perp}(\omega)$ its intensity profiles measured with parallel and crossed polarizers, respectively. Write $I_{rs}^0 = I_{rs}^{\parallel} - (4/3)I_{rs}^{\perp}$ and normalize both $I_{rs}^0(\omega)$ and $I_{rs}^{\perp}(\omega)$ so that

$$\int_{-\infty}^{+\infty} I_{rs}^{0,\perp}(\omega)\eta(\omega)d\omega = 1, \quad (1)$$

where $\eta(\omega) = [1 + \omega/(\omega_e - \omega_{rs})]^{-4}$, ω_e being the excitation frequency and ω_{rs} the frequency of the vibrational transition (in most cases η may be substituted by unity). The reorientation correlation function $\chi_2^{rs}(\tau)$ for the anisotropic part of the transition polarizability tensor \mathbf{A}^{rs} is then given by

$$\chi_2^{rs}(\tau) = \int_{-\infty}^{+\infty} \eta(\omega)I_{rs}^{\perp}(\omega) \exp(i\omega\tau)d\omega/K_{rs}(\tau), \quad (2)$$

where

$$K_{rs}(\tau) = \int_{-\infty}^{+\infty} \eta(\omega)I_{rs}^0(\omega) \exp(i\omega\tau)d\omega. \quad (3)$$

The validity of Eq. (2) is based on these assumptions:

(a) Raman scattering is incoherent (see Ref. 5), (b) the vibration-rotation interaction is sufficiently weak, (c) the statistical cross correlation between the reorientation process and any scalar broadening mechanism is negligible, and (d) the shape fluctuations of the polarizability tensor do not contribute significantly to the width of the band.

It has been shown^{4,5} that the above method is not

sensitive to the presence of other broadening mechanisms such as the intra- and intermolecular vibrational energy transfer, the adiabatic vibrational frequency shifts⁶ (VFS), and the translational diffusion.⁷ The invariance of Eq. (2) with respect to VFS is of enormous importance since even considerable shifts and splittings of the band do not affect the results, provided (as is often the case) they are not accompanied by any substantial variation of \mathbf{A}^{rs} . Another pleasant feature of Eq. (2) is its insensitivity to the choice of the center of the band (i.e., the frequency origin).

It is of some interest to notice the structure⁴ of K_{rs} :

$$K_{rs}(\tau) = V_{rs}(\tau)\Phi_{rs}(\tau)D(\tau) \exp(-i\Delta\tau), \quad (4)$$

where V_{rs} comprises the vibrational energy transfer and can be approximated by the formula $V_{rs}(\tau) = \exp(-|\tau|/\tau_r) \exp(-|\tau|/\tau_s)$, τ_i being the mean lifetime of the molecule in the i th vibrational state,⁸ Φ_{rs} is the Fourier transform of the density function of the adiabatic vibrational frequency shifts, D involves the diffusion effects,⁷ and Δ is the error in the estimated frequency of the center of the band.

Combining Raman data with the ir evidence one can arrive (in principle) at the vector reorientation correlation function $\chi_1^{rs}(\tau)$ characterizing the reorientation of the transition dipole moment \mathbf{d}^{rs} . Since the scalar relaxation processes are identical for ir and Raman,

$$\chi_1^{rs}(\tau) = \exp[i(\Delta_R - \Delta_{ir})\tau] \int_{-\infty}^{+\infty} I_{rs}^{ir}(\omega) \times \exp(i\omega\tau)d\omega/K_{rs}(\tau), \quad (5)$$

where $I_{rs}^{ir}(\omega)$ is the normalized ir band shape and $(\Delta_R - \Delta_{ir})$ is the error in the mutual fit of the ir and Raman frequency scales (it is rather difficult—though not impossible—to eliminate this instrumental error).

My final remark regards the application of Eq. (2) to the molecules which undergo internal rotations. In this case there arise four possibilities: (1) The band belongs to a long-range torsional motion. The vibration-rotation interaction is then usually rather strong so that the results are not reliable. (2) The band is a heterogeneous mixture of several bands belonging to different conformers. In this case nothing can be done unless the transition polarizability tensors are nearly identical. (3) The band can be assigned to a single conformer. $\chi_2^{rs}(\tau)$ then describes the reorientation properties of this particular species. (4) The band can

be characterized as a localized vibration of a rigid molecular fragment. The function $\chi_2^{rs}(\tau)$ then refers to the reorientation of this single fragment. This is a most inviting possibility especially in connection with the study of large molecules and polymers.

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¹ A. V. Rakov, *Opt. Spektrosk.* **7**, 202 (1959).

² R. G. Gordon, *J. Chem. Phys.* **42**, 3658 (1965); **43**, 1307 (1965); **44**, 1830, 3083 (1966); *Advan. Mag. Resonance* **3**, 1 (1968).

³ S. Bratos and E. Marechal, *Phys. Rev. A* **4**, 1078 (1971).

⁴ S. Sýkora, U. S. Clearinghouse Fed. Sci. Tech. Inf. No.

724330 (1971). A revised version of this report (including a compact derivation of the results mentioned in this note) will be mailed to anybody interested in it.

⁵ F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.* **56**, 404, 413 (1972).

⁶ I am indebted to Prof. N. Sheppard for drawing my attention to this problem.

⁷ For some reason this mechanism is never explicitly mentioned in the literature. It arises from the space dependence of the excitation wave and the corresponding correlation function can be evaluated by the general formula $D(\tau) = \langle \exp[i\mathbf{k} \cdot (\mathbf{R}(t+\tau) - \mathbf{R}(t))] \rangle$, where \mathbf{k} is the wave vector of the incident light and \mathbf{R} is the position vector of the molecule.

⁸ Practically identical equation has been derived by H. Morawitz and K. B. Eisenthal, *J. Chem. Phys.* **55**, 887 (1971). Their derivation is however only seemingly more rigorous since it is based on equally intuitive and simplifying assumptions.

Paramagnetic Moments for All Crystal Field Strengths of Octahedral Mn^{3+} Complexes*

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A general calculation of paramagnetic susceptibilities has been carried out for d^4 ions in octahedral fields using complete crystal field energy level calculations and limited spin-orbit interaction. The molar susceptibility χ was obtained by direct Boltzmann averaging of the magnetic moments $\mu_i = -\partial E_i / \partial H$, evaluated by numerical differentiation, where E_i is the value of the i th energy level and H is the magnitude of the magnetic field.¹⁻⁴ Spin-orbit energies must be included to obtain the necessary precision for the E_i . The effective magnetic moment μ_{eff} is determined in units of Bohr magnetons μ_B by $\mu_{\text{eff}} = (kT\chi / N\mu_B^2)^{1/2}$, where k is Boltzmann's constant, N is Avogadro's number, and T is the temperature.³ Since the averaging is not simplified by assumptions regarding the arrangements of energy levels, the calculated susceptibilities are restricted only by approximations employed in the energy calculations. Approximations in this calculation are the use of strict cubic symmetry, neglect of non- d character in the state vectors, neglect of spin-orbit interaction between multiplets, and the evaluation of Zeeman matrices over lower crystal field states. With this approach, χ and μ_{eff} can be calculated for all values of the crystal field strength $\Delta = 10Dq$, including regions where the usual approximations are not valid.¹

Matrices of a Hamiltonian consisting of crystal field, electrostatic, and spin-orbit interactions were constructed on the complete d^4 free ion S, L, J basis by the methods of Racah and Judd.^{5,6} Formulas for the three- j and six- j symbols were taken from Rotenberg *et al.*, and reduced matrix elements were obtained from Nielson and Koster.^{7,8} The matrix elements were expressed in terms of the Racah parameters A, B, C , the single electron spin-orbit parameter ζ , and the crystal field strength Δ . Matrices of the Zeeman term $\mu_B \mathbf{H} \cdot (k\mathbf{L} + g\mathbf{S})$ where k is the orbital reduction factor, were constructed and diagonalized over eigenvectors of the Hamiltonian

corresponding to eigenvalues less than 11 000 K above the ground level.⁹ Reduction with respect to the C_4^d double group produced matrices no larger than seven by seven.

Energy levels within 2000 K of the ground level and the corresponding magnetic moment are plotted against Δ in Fig. 1. The values used for B, C , and ζ were taken

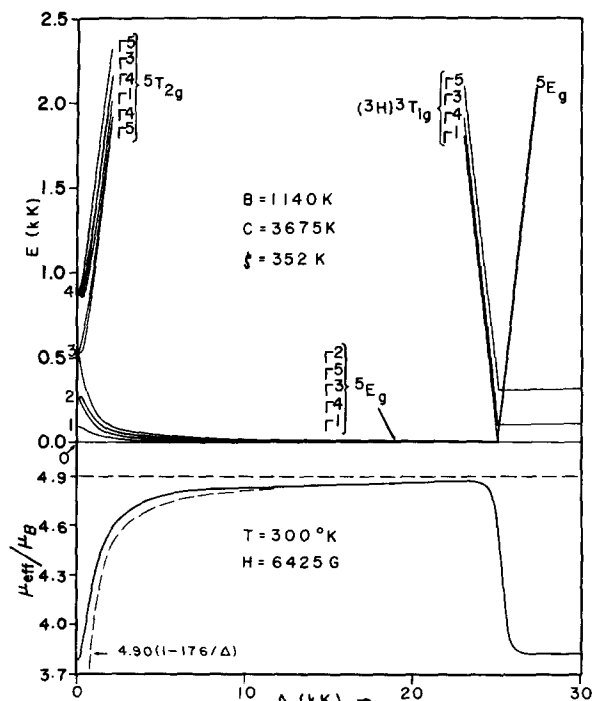


FIG. 1. Effective magnetic moment and low-lying energy levels of a d^4 ion in an octahedral crystal field as functions of the crystal field strength Δ . Parameters B, C , and ζ have Mn^{3+} values taken from Refs. 2 and 9, and the orbital reduction parameter is $k=1.0$. Integers along the upper left axis are the J values for 5D .